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USE OF TRI-N-BUTYLTINS IN THE ATLANTIC REGION 1986/87

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USE OF TRI-N-BUTYLTINS IN THE ATLANTIC REGION 1986/1987

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ABSTRACT

The use pattern of Tri-n-butyltin compounds in the Atlantic Region for the survey year 1986/87 was assessed. Major use areas and quantities allocated to each of these areas were determined.

RÉSUMÉ

L'emploi des composés de Tri-n-butylétain dans la Région de l'Atlantique a été évalué pour l'année 1986/87. Les zones d'utilisations principales et les quantités allouées à chacune de ces zones furent déterminées.

ACKNOWLEDGEMENTS

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Seatech Investigation Services Ltd. conducted the Tri-n-butyltin use pattern assessment under contract to Environment Canada. This report is based on the contractor's report describing survey results.

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1.0 INTRODUCTION

Tri-n-butyltins (TBTs) belong to the organotin class of chemicals which, in 1987, were included in the List of Priority and Candidate Chemicals (Category 3 of Priority Chemicals) developed under the Environmental Contaminants Act. This list included substances which:

> "may pose a significant danger to human health or the environment and about which further detailed study or information - for example toxicology, amounts used, or concentrations in the environment - is necessary."

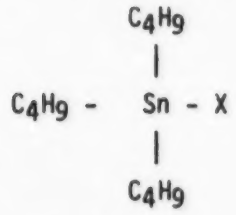
TBTs have a variety of biocidal applications in Canada. Recently, concerns have focused on the potential for TBTs to cause adverse environmental impacts, particularly in the marine environment. Aquaculture, an important growth industry in the Atlantic Region, is an area of particular sensitivity. It has been demonstrated that, at low concentrations, tri-n-butyltin oxide (TBTO) is lethal to the larvae of the blue mussel (Mytilus edulis) (Beaumont and Budd, 1984), affects shell growth of the oyster (Crassostrea gigas) (Alzieu et al., 1981; Waldock and Thain, 1983), and may affect reproductive success in the gastropod (Nucella lapillus) (Bryan et al., 1986).

TBTs have been used in marine antifoulants, wood preservatives (including lobster trap preservatives), cooling water slimicides, and materials germistats. Detailed use pattern information, however, has never been compiled in the Atlantic Region. In order to better identify and assess potential problems arising from the use of these substances in the region, Environmental Protection, Conservation and Protection, Environment Canada, initiated a TBT use pattern assessment in October of 1987. The specific objectives of the assessment were (1) to identify the significant uses of TBT in the region and (2) to determine the quantities of TBT allocated to each of these uses.

2.0 TRI-N-BUTYLTIN USES

2.1 Background

Tri-n-butyltins belong to the class of chemicals known as organotins. They are chemically characterized by a tin (Sn) atom covalently bonded to three butyl (C_4H_9) moities, as described by the following general structural formula:



The TBTs in commercial use in Canada include tri-n-butyltin oxide (TBTO), tri-n-butyltin chloride (TBTCl), tri-n-butyltin fluoride (TBTF), tri-n-butyltin maleate (TBT maleate), and tri-n-butyltin methacrylate (TBT methacrylate).

2.2 Antifoulants

Marine fouling is the attachment of marine organisms, animal or plant-type, to a surface immersed in seawater (Evans, 1970). Fouling produces roughness on a ship's hull, increasing turbulence and drag which can slow a vessel down. This may have potentially serious economic consequences since, if fouling is not prevented, fuel consumption and costs can significantly increase (Champ and Pugh, 1987).

Marine antifouling paints were developed to prevent or reduce fouling. These paints, which release small amounts of biocides at the surface to kill fouling organisms, are of three types - free association, ablative, and copolymer. Free association paints and ablative paints contain biocides which are loose in the paint, and are characterized by a life expectancy of 2 years. Copolymer paints, which contain biocides chemically bonded to the polymer have a life expectancy of 5 years (Champ and Pugh, 1987).

TBTs have been used as bioactive agents in antifoulant paint because: (1) they provide superior protection over longer periods of time than other agents; (2) they do not promote corrosion; and (3) long-term degradation products are relatively non-toxic (Hoffman et al., 1978).

To prevent fouling of nets used in aquaculture operations, TBTs have also been used as antifoulants in net dip products (Environment Canada, Agriculture Canada, Fisheries and Oceans Canada, 1987).

2.3 Wood Preservatives

Wood preservatives are used to protect wood from fungal and insect attack. Desirable properties in preservatives are that they must penetrate the wood and be uniformly distributed, be resistant to leaching, and not materially alter the properties of wood (Evans and Karpel, 1985). TBTs have been reported to be effective bioactive agents in these materials (National Research Council Canada, 1985).

2.4 Materials Germistats

Materials biocides or germistats are used to protect textiles of natural fabrics (such as cotton, silk, or wool), and leather from attack by micro-organisms. TBTO is effective against a wide range of fungi and bacteria, such as Chaetomuin globosum on cotton, and has been used as the active ingredient in a number of materials germistats (Evans and Karpel, 1985).

2.5 Slimicides

Slimicides are used to control slime forming bacteria and fungi, particularly in the pulp and paper industry. In this sector, slime, which consists of a mixture of micro-organisms and pulp, can interfere with paper production by clogging equipment and can impair paper quality. TBT compounds are effective slimicides (Evans and Karpel, 1985).

3.0 METHODS

The Atlantic Region use pattern assessment was conducted in three phases.

3.1 Phase I

Phase I consisted of the preparation of a preliminary information package on uses of TBT in Canada. General information on possible uses of TBT was compiled from published literature, government reports, and knowledgeable contacts. This included a listing of TBT products registered under the Pest Control Products Act complete with product names, use type, TBT derivatives, and percent active ingredients.

3.2 Phase II

Phase II involved the collection of regional use information. To obtain use quantity data, and more details on use categories, several different information sources and approaches were used, depending on the particular use and degree of detail required. Wherever possible, information was obtained from existing data collected by government agencies, including Agriculture Canada, Environment Canada, and Statistics Canada. Where data gaps existed, information was solicited from industry contacts.

The main use of TBT and the most important, from an environmental perspective, was expected to be that in antifouling paints. Since this was also the area where the least amount of information was available from government sources, most survey resources were concentrated in this area. Potential TBT paint formulators and distributors as well as end users, including forty-two shipyards, were identified from trade and telephone directories and contacted to determine: (1) the TBT paint products in use; (2) the market sector; (3) the geographic distribution; and (4) the quantities sold or used.

Data on commercial marine and military use was obtained from end users. Industry estimates were obtained for comparative purposes. Since a survey of end users of pleasure craft paint was impractical, pertinent information

was obtained from industry estimates of total regional use, and from Statistics Canada data on the number of pleasure craft per province. Expected future use information was also solicited.

Information on the use of antifoulant net dips was obtained from a 1987 Agriculture Canada survey of TBT net dip stocks in the region.

Data on TBT use in lobster trap preservatives was obtained from regional formulators.

Information on TBT use in products registered under the Pest Control Products Act, i.e. wood preservatives, materials germistats, and cooling water slimicides, was obtained from the National Pesticides Registrants Survey. This survey, conducted yearly and jointly by Environment Canada and Agriculture Canada, consists of the collection of information on registrant reported sales by provinces for each registered product. The information was collected as confidential business information and to protect the confidentiality, TBT data obtained from this source could be reported in summary form only.

3.3 Phase III

Phase III consisted of data evaluation.

4.0 RESULTS AND DISCUSSION

The survey identified a total of 3,440 kg TBT in use in the region in 1986/87. The use categories are as follows: antifoulants - 53%; lobster trap preservatives - 24%; and wood preservatives/materials germistats/cooling water slimicides - 23% (Figure 1).

Note: Where TBT quantities are reported, volumes refer to total active ingredient.

4.1 Antifoulants

4.1.1 Antifouling Paints

Sixteen individual TBT paint products were found to be in use in the region (Table 1). Twelve contained TBTO and four contained TBTF. Formulations in the products varied, ranging from 0.4 to 22.1% active ingredient for TBTO, while the TBTF formulations were all approximately 15% active ingredient. Of the sixteen products identified, two contained TBT in the copolymer form. These were for pleasure craft use.

TBT antifouling paints represented 5-10% of the total antifouling paint consumption for commercial marine/military use. This figure was substantially larger for pleasure craft, where TBT paints accounted for 60% of the total antifouling paint usage.

In 1986/87, a total of 1725 kg of TBT was used in antifouling paints. Table 2 provides a breakdown of the TBT use in antifoulant paints according to market sector and province. The largest volumes of TBT in paints were used in the commercial marine sector (57%), followed by pleasure craft/miscellaneous (35%), and the military sector (8%). Assuming active ingredient comparisons and total product comparisons are equivalent, this agrees closely with US Environmental Protection Agency 1985 use pattern data for TBT antifouling paints which reported 59.3% use in the commercial sector, 33.4% for recreational use, 3.2% for military purposes, and 4.1% unknown (USEPA, 1987).

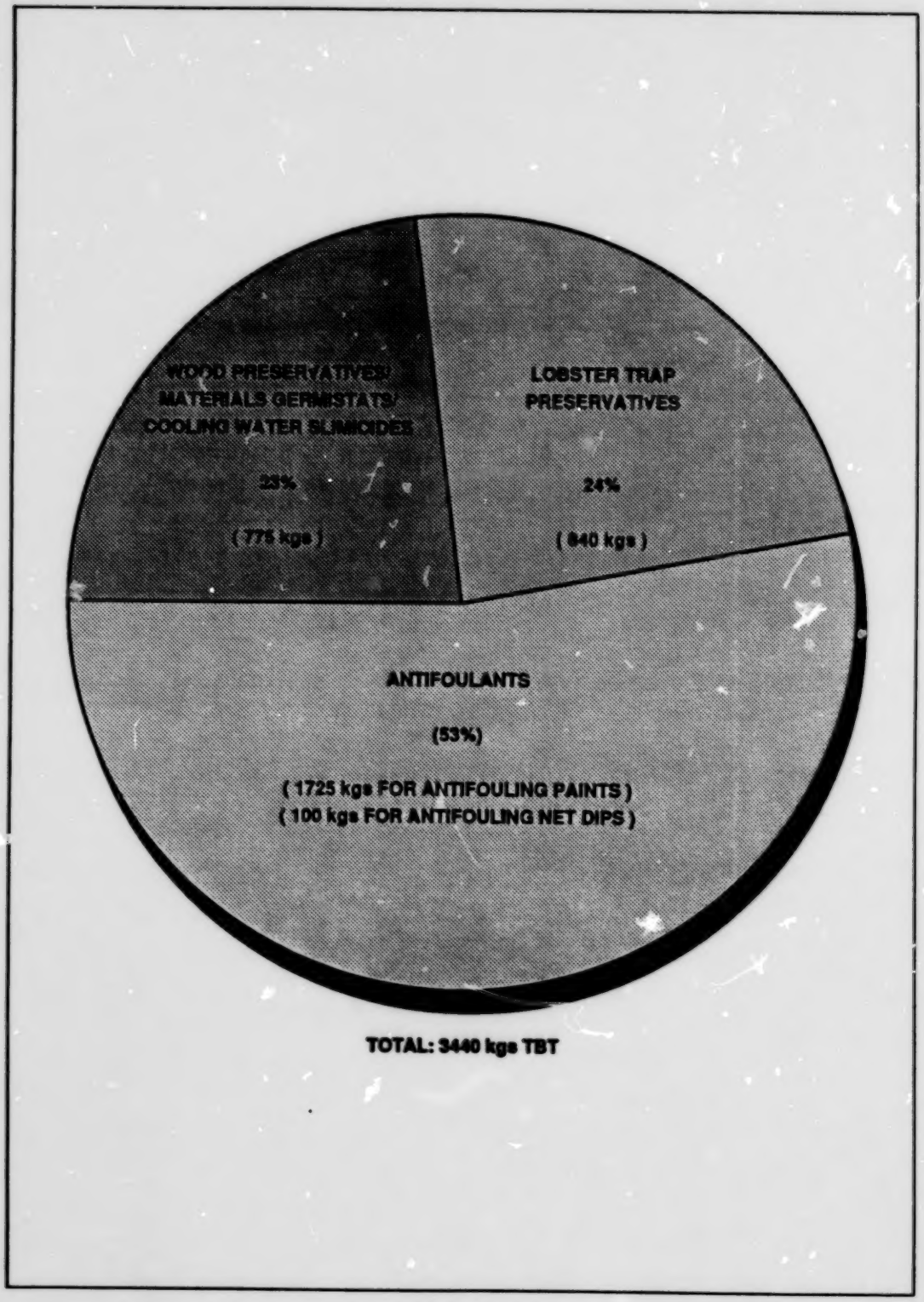


Figure 1 Atlantic Region Tri-n-butyltin Use Pattern — 1986/87

TABLE 1 TBT ANTIFOULING PAINTS IN USE, ATLANTIC REGION - 1986/87

Paint
Navicote Vinyl Antifouling - Red
Devran 222 Light Blue Antifouling
ABC 2 Red Antifouling
Speedkote Antifouling Black
Interspeed BWA101
Interlux Micron 25
Interlux Tri-Lux TBTF
Interlux Micron 33
Interspeed BLA220
Interspeed BJA450
Interspeed BCA300
Interspeed BLA200
Matchless Super Marine Tri-antifouling Paint - 1
Fisherman's Brand #3054
Red Copper Antifoulant #5027
Red Copper Antifoulant #5029

TABLE 2 TBT USE IN ANTIFOULING PAINTS, ATLANTIC REGION - 1986/87

Market Sector	Amount per Province (kg TBT)					
	Nova Scotia	Newfoundland	Prince Edward Island	New Brunswick	Total	Percentage
Commercial Marine	590	330	65	0	985	57
Pleasure Craft/ Miscellaneous*	425	70	40	70	605	35
Military	135	0	0	0	135	8
TOTAL	1 150	400	105	70	1 725	

* Includes small fishing craft paint usage

The largest quantity of TBT paints was used in Nova Scotia, followed by Newfoundland. Prince Edward Island and New Brunswick consumed comparatively minor amounts. Surprisingly, no TBT paint use was reported in the commercial marine sector in New Brunswick. As location specific information was obtained for commercial marine/military paint usage, a figure illustrating the geographic distribution of TBT usage in these combined areas was prepared (Figure 2). Location specific information for pleasure craft usage was not available and therefore could not be incorporated into the figure.

Table 3 compares triorganotin data for antifouling paints for different geographic areas. As a rough approximation, based on estimates made by the paint formulators and distributors contacted in this survey, the Atlantic Region accounts for 10% of the national use. The largest proportion of the TBT antifouling paint use in Canada occurs on the Pacific Coast and the Great Lakes. The comparatively lesser use in the Atlantic Region may be related to differences in water temperatures as well as number of vessels.

4.1.2 Antifouling Net Dips

A single TBT net dip product was identified in use in the Atlantic Region in aquaculture for fin fish farming operations. The product, imported from the United States, was Flexguard Waterbase Preservative, containing 3% TBTO. Approximately 100 kg TBT was used in 1986/87.

4.2 Lobster Trap Preservatives

Three lobster trap preservatives containing TBTO were used in the region. These products, containing between 1.5 and 2.5% TBTO, were: Nowrm (Trap Dip); Clear Trapsaver; and Black Trapsaver. In 1986/87 the total use of TBT in this category was estimated at 840 kg, which represented the second major use category of TBTs in the region. This was a significant finding since, prior to the survey, lobster trap preservatives were expected to be a minor use area of TBTs.

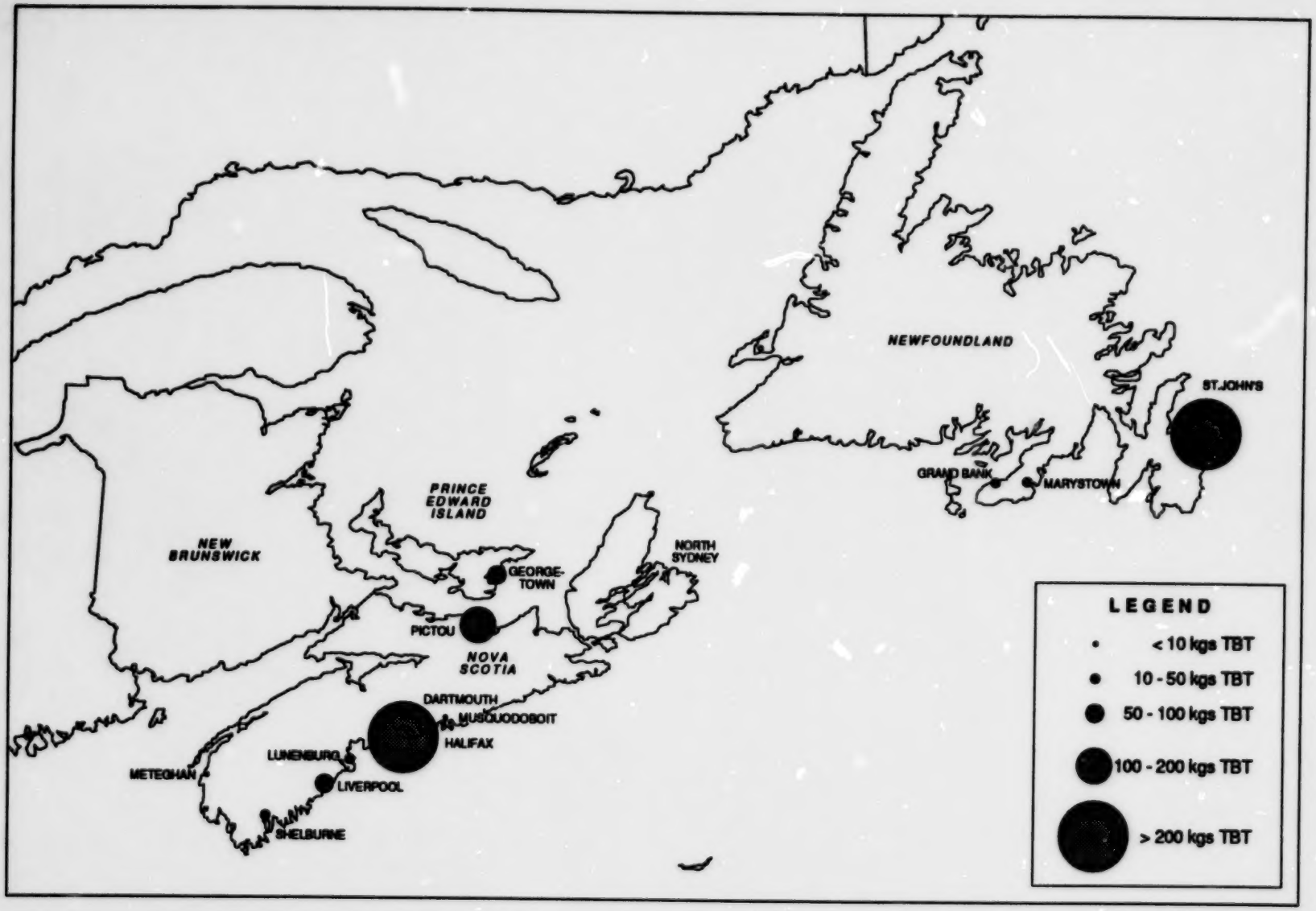


Figure 2 Commercial / Military TBT Antifouling Paint Use by Port in The Atlantic Region — 1986/87.

TABLE 3 TRI-ORGANOTIN USE IN ANTIFOULING PAINTS

Location	Active Ingredient	Annual Use (kg)	Reference
World Use	Tri-n-butyltin and Triphenyltin	2 - 3,000,000	Evans and Karpel (1985)
United States	Tri-n-butyltin	110 - 140,000	Champ and Pugh (1987)
Canada	Tri-n-butyltin	18,000	This study
Atlantic Region	Tri-n-butyltin	1,725	This study

4.3 Wood Preservatives/Materials Germistats/Cooling Water Slimicides

Products registered in Canada in 1986/87 as wood preservatives, materials germistats and slimicides are listed in Table 4. This list includes all products registered under the Pest Control Products Act (PCPA), and not just those distributed and used in the Atlantic Region.

Of the 21 wood preservatives registered, all contained TBTO in formulations ranging from 0.075% to 3.45%. Products were registered for various uses including: sap stain inhibitors for use on fresh cut lumber; preservatives for use on wood decks, fences, and sidings; and preservatives/water repellants for treating exterior millwork, doors, window sash components as well as outdoor furniture. (This list excludes lobster trap preservatives, since they were not PCPA registered.) In products which contained TBTO in concentrations less than 1%, TBTO functioned as an in-can preservative (Jones, 1988).

Of the 15 materials germistats listed, 12 contained TBTO in concentrations ranging between 0.098% and 10.0%, one contained 21% TBT maleate, another contained 4.39% TBT chloride, while another contained 40.1% TBT methacrylate. The products were registered for use as bacteriostats, fungistats, or germistats in the manufacture of textiles, leather goods (i.e. footwear), casein, water based emulsions such as latex emulsion paints, and water-based adhesives.

The 12 cooling water slimicides listed contained TBTO in concentrations ranging from 0.6-5.0%.

A total of 775 kg TBT was used in these combined areas in the region. Overall, TBT compounds in wood and materials germistats, as opposed to cooling water slimicides, accounted for the vast majority of use.

Approximately 290 kg were used in Nova Scotia, 355 kg in New Brunswick and 130 kg in Newfoundland and P.E.I. (combined to protect the confidentiality of the information).

TABLE 4 TBT CONTAINING PRODUCTS
WOOD PRESERVATIVES/MATERIALS GERMISTATS/COOLING WATER SLIMICIDES

	Pest Control Products Act Registration Number
Wood Preservatives	
Wood Preservative Clear	16708
Pentox Primer Sealer Wood Preserver Green	5565
CCC Wood Preservative	11331
Wolman Outdoor Wood End Cut Preservative	15935
Osmose Wood Preservative for End Cuts	18972
Alchem 4135 Fungicide Sap Stain Inhibitor	13778
Weather Screen 704	16795
Weather Screen 707	16796
Weather Screen 709	16797
Weather Screen 713	16798
Weather Screen 716	16799
Weather Screen 717	16800
Weather Screen 723	16801
Weather Screen 726	16802
Weather Screen 911	16803
Weather Screen 913	16804
Pittsburgh Paints Exterior Stain and Wood Preservative	19591
Pilt Plus	19539
Pilt Plus	19540
Pilt Plus	19541
Pilt Plus	19543
Materials Germistats	
Textile/Paper/Leather Germistats	
Sanitized Brand 817	12879
Sanitized Brand RB-475	12880
Sanitized Brand OA-P	13538
Ultra-Fresh UDD Cationic Germistat	12891
Ultra-Fresh UDD Nonionic Germistat	12895
Ultra-Fresh 300 DD Nonionic Germistat	12895
Ultra-Fresh U Nonionic Germistat	12896
Ultra-Fresh 300 DD Cationic Germistat	12897
Ultra-Fresh 300 DD Nonionic Germistat	12901
Ultra-Fresh 300 Cationic Germistat	12902
Ultra-Fresh U Cationic Germistat	12904
Ultra-Fresh SN Germistat	16145
Ultra-Fresh DM-40	12900
Ultra-Fresh DM-50 N Germistat	14498
Biosperse 219	15593

Cont'd

TABLE 4 (Cont'd

	Pest Control Products Act Registration Number
Cooling Water Slimicides	
Alchem 7328	15515
Betz Slimicide J-12	13486
ML-15	15525
Dearcide 717 Cooling Water Microbistat	13189
Dearcide 703 Cooling Water Microbistat	13350
Dearcide 700 Cooling Water Microbistat	13931
Biosperse 201	14565
Mogul AG-471	13488
Mogul AG-472	14592
Formula 3475	13500
Formula 3470	18129
Virginia Algae-cide No. 5	13503

4.4 Projected Use

The uses of many TBT products are currently being evaluated for registration under the Pest Control Products Act. For these products, use patterns are expected to change somewhat in the near future.

The Agriculture Canada registration requirement of TBT antifoulants will likely significantly affect this use category. Some formulators surveyed reported that, rather than seek registration, they intended to discontinue manufacturing certain TBT products. Other formulators indicated their intention to seek registration for TBT antifoulant paints, but these paints would be reformulated with a reduced TBT content. The net result of these changes is expected to be a substantial reduction in the use of TBT in antifouling paints. In addition, the use of TBT net dips is expected to be eliminated, since Agriculture Canada prohibited such use in 1987.

Future use of TBT lobster trap preservatives is also expected to be reduced to zero. As the products used in the region were not registered control products, in 1988 Agriculture Canada disallowed their continued use.

As no regulatory changes are anticipated in the near future for the use of TBT wood preservatives, materials germistats, or cooling water slimicides, no major changes in use pattern for these products are anticipated.

4.5 Data Evaluation

Survey results obtained from antifouling paint end users were compared with formulator and distributor TBT paint use estimates. Agreement was reasonable (within 20%), suggesting that the reported data are representative of actual use. The data on lobster trap preservatives as well as the data on wood preservatives/materials germistats and cooling water slimicides were based on formulator/registrant reported yearly sales data. Assuming that yearly sales are equivalent to yearly use, these data are also expected to reasonably represent actual use. The antifouling net dip data, however, is a rough estimate based on the assumption that the

stocks reported at the time of the ban approximated yearly use and, therefore, is not as representative as the above information. Use of TBT as a net dip was relatively minor, however, and should not significantly affect overall TBT use estimates.

While this survey may not include all possible uses of TBT products in the region, it is believed that all significant uses were identified. The assessment should, therefore, provide a reasonable picture of TBT use in 1986/87 in the Atlantic Region.

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